PATENTTI- JA REKISTERIHALLITUS
NATIONAL BOARD OF PATENTS AND REGISTRATION

RG

PCT/FI 99 / 00288

5

Helsinki 21.04.99

09 / 647458

#6 3-9-01 J. Artis

REC'D 16 JUN 1999
WIPO PCT

E T U O I K E U S T O D I S T U S
P R I O R I T Y D O C U M E N T

Hakija
Applicant

HELSINKI UNIVERSITY
LICENSING LTD OY
Helsinki

Patenttihakemus nro
Patent application no

980781

Tekemispäivä
Filing date

03.04.98

Kansainvälinen luokka
International class

G 01N

Keksinnön nimitys
Title of invention

"Method and apparatus for analysis of gas compositions"
(Menetelmä ja laite kaasuseosten analysoimiseksi)

Täten todistetaan, että oheiset asiakirjat ovat tarkkoja jäljennöksiä patentti- ja rekisterihallitukselle alkuaan annetuista selityksestä, patenttivaatimuksista, tiivistelmästä ja piirustuksista.

This is to certify that the annexed documents are true copies of the description, claims, abstract and drawings originally filed with the Finnish Patent Office.

Pirjo Kaila
Tutkimussihteeri

PRIORITY DOCUMENT
SUBMITTED OR TRANSMITTED IN COMPLIANCE WITH RULE 17.1(a) OR (b)

Maksu 255,- mk
Fee 255,- FIM

Osoite: Arkadiankatu 6 A
Address: P.O.Box 1160
FIN-00101 Helsinki, FINLAND

Puhelin: 09 6939 500
Telephone: + 358 9 6939 500

Telefax: 09 6939 5204
Telefax: + 358 9 6939 5204

METHOD AND APPARATUS FOR ANALYSIS OF GAS COMPOSITIONS

Background of the Invention

Field of the Invention

The present invention relates to spectroscopic analysis of gas compositions in sealed containers. More specifically, the invention relates to a non-invasive method for selectively analysing gas-mixtures enclosed in a spacing between two glass sheets, such as between the panels of a window glazing unit. The present invention also concerns a modular, portable apparatus for analyzing the performace of gas-filled window glazing units.

Description of Related Art

Filling gases with low thermal conductivity, e. g. argon, krypton and xenon, as well as low imissivity coatings are often used for a considerable reduction of heat transfer in window glazing units. The performance of the glazing units dramatically depends on the gas present in the spacing. For example, xenon and krypton provide much better insulation than argon. Also, as the rim seal is not perfectly leak tight, part of the filling gas can diffuse out and air can diffuse into the spacing, resulting in decreasing insulation performance. In order to predict the storage and operating lifetimes, there is a need for precise analysis of the gas mixture composition during manufacturing, storage and use. When the window fillings of existing constructions are to be tested, the movability of the measuring unit is of great importance.

The sum pressure of a gas mixture contained in a gas-filled glazing unit is always atmospheric which means that numerous known methods and devices for analyzing low-pressure gases are not applicable. Known gas analyzers employing mass-spectrometry and gas-chromatography are not suitable because they require physical contact with analyzed gas volume. Methods based on infrared and Raman spectroscopy are not applicable in the case of noble gas atoms because they essentially probe vibrational

frequencies of molecules. Laser spectroscopic methods are not suitable because of complicated and expensive equipment employed. Direct measurements of the absorption spectra are also impossible to utilize in movable devices because the absorption lines of the noble gases occupy the vacuum ultraviolet spectral region not transmitted by the window glazing panels.

There are a number of known methods for spectroscopically analyzing the performance of gas-filled electronic lamps. In particular, a method utilizing optogalvanic phenomenon (US Patent No. 4,939,926) has been suggested for determining the performance of sealed rf discharged lamps at low pressure. The known method cannot be directly utilized for atmospheric pressure windows. In an embodiment described in the patent, a broad band ultraviolet-visible source is employed, which prevents the use of the method for selective measurements. In order for the optogalvanic approach to provide selectivity, a high-intensity tunable laser source should be used, which prevents the method from coming to portable realization.

DE Published Patent Application No. 195 05 104 discloses a method and an arrangement for testing the purity and pressure of gases for electrical lamps. For the measurements both pressure dependent and independent emission lines are obtained. The prior art technology is designed for detection of impurities in electronic lamps, especially in those filled with noble gases. An external hf-excitation source with one electrode is used, and the lamp electrode acts as the other electrode. As regards the discharge excitation, the device is not suitable for atmospheric-pressure sealed containers because the measurement of argon pressure is insensitive when the pressure exceeds 10 kPa. Discharge in extensive volume requires high power of the source which means that portable realization is problematic.

A non-invasive pressure measuring device described in US Patent No. 5,115,668 is used for estimating the luminance of an externally induced, high-frequency glow discharge of a gas in a lamp. Comparison of the measured luminance with calibrated luminance vs. pressure data provides the pressure for the gas. The device employs an indirect method for pressure dependence of the luminance without any normalizing procedure, which makes it sensitive to geometrical re-arrangement so that the device is not really transportable. The

method uses stable rf excitation and applies to a narrow field of application, i. e., low-pressure lamps, and it cannot be applied to atmospheric pressure sealed containers. The device measures the light in integral without wavelength analysis which means that it is not selective to different elements.

US Patent No. 5,570,179 discloses a measuring sensor and a measuring arrangement for use in the analysis of gas mixture, consisting of a chamber with transparent window(s) and arranged gas flow, two electrodes on the opposite side of the chamber to apply high alternating voltage to the gas flow, and light detector(s) to measure the intensity of radiation emitted through the chamber window in some selected spectral region. The device is designed mainly for surgical use in hospitals. The method is not non-invasive so that it is not applicable for sealed containers like gas-filled window glazing units. The use of two electrodes is impossible in a window units possessing an inner conducting layer.

There are a number of methods and devices specially created for estimating the performance of window glazing units. A known chemical gas monitor for detecting a leak of the window panel (cf. US Patent No. 4,848,138) uses chemicals, which are reactive with the constituents of air but not reactive with noble gases. The method requires special reconstruction of the window because the virtual chemical must be inserted during window manufacturing, and it cannot be used for existing constructions.

A known non-destructive method for determination of the rare-gas content of highly insulating glazing units (DE Published Patent Application No. 195 21 568.0) allows for the determination of the leak of air into the window spacing, at least, for krypton and xenon. The determination of the relative amount of the noble gas is based upon measuring the sound velocity in the gas filling. The method is, however, mainly applicable to stationary measurements because it requires precise control of measurement condition (temperature, spacing distance, etc.), which makes any portable realization very questionable and field measurements impossible. Also, the method is insensitive to argon filling, which is one of the most important in the area. The method is inselective to different noble gases so that it is unable to distinguish, for example, a mixture of krypton with air from proper filling with argon.

To complete the survey of related art, a method of determining the percentage gas content of an insulating glass window unit is known from US Patent No. 5,198,773. The prior method is based on applying a voltage to opposite panes of the unit, progressively increasing the voltage, monitoring the voltage, recording the value of threshold discharge voltage, and converting the magnitude to percentage gas content between the panes. The method is directed to recognizing the percentage content of some given gas (e. g. argon or sulfur hexafluoride) between gas panel, and it is impossible to apply it for a window unit of unknown filling. In other words, the prior method is not selective to different noble gas fillings. Also, the necessary use of two electrodes prevents the method from measuring units with conducting inner layers, which are commonly used now to improve insulation performance of the production.

Summary of the Invention

It is an object of this invention to eliminate the problems relating to the prior art and to provide a novel method for selective identification of gas components present in a gas or gas mixture.

It is another object of the invention to provide a compact, easily movable and inexpensive device, which is suitable for selective identification of gas components typical for insulation window glazing units, i. e., argon, krypton, xenon and air.

These and other objects, together with the advantages thereof over known processes, which shall become apparent from specification which follows, are accomplished by the invention as hereinafter described and claimed.

The present invention is based on the concept of discharging the spacing between the panels of the window glazing unit by applying rapidly alternating electrical field to the spacing between the panels of the window glazing unit. To achieve a discharge, a grounded counter-electrode is used. In particular, the present invention comprises creating a local excitation of the gas in a glazing unit by using an electrode having a specific design, while the inner conducting layer of the glazing unit may serve as the counter-electrode. The

emitted light of the discharge is collected from a collection area larger than the emission area, analyzed in different spectral intervals and compared with the integral value of the discharged light.

The localization of the discharge in the vicinity of the end of an electrode having a small end (e.g. a needle-like electrode) allows for collection of the emitted light without routine adjustment of the optical system.

According to the present invention, the apparatus for non-invasive analysis of, e.g., gas-filled window glazing units comprises means for locally applying the rapidly alternating high voltage to the spacing of the window glazing unit to achieve local emission and means for collecting and transporting emitted light. Further there are means for determining the integral intensity of the emission, means for determining the intensity of a spectral interval corresponding to the gas component of interest and means for calculating the ratio between the intensity of the spectral interval and the integral value of the intensity.

More specifically, the present invention is mainly characterized by what is stated in the characterizing part of claim 1.

The apparatus according to the invention is characterized by what is stated in the characterizing part of claim 9.

Considerable advantages are achieved by the invention. Thus, factory-adjusted lenses can be used to collect the light from the discharge, and the collected light can be transported to light detectors by using fiber optics, which eliminates influence of instability of the discharge geometry.

According to a preferred embodiment, a modular apparatus is provided, in which the electrode used for local application of rapidly alternating high voltage to the spacing of the window glazing unit and the lens or mirror used for collecting the emitted light are arranged in one portable unit (remote sensor unit) which easily can be transported to the vicinity of the glazing unit which is to be tested. The remaining part of the apparatus can be

mounted into a, likewise movable, separate processing unit. If desired, the remote sensor unit can further be provided with means for displaying the obtained information about the performace of the window glazing unit, so as to provide the person testing the window to obtain the necessary data for evaluating the performance of the window. An additional light detector can also be fitted in the remote sensor unit and connected to the processing means with an additional electrical line, a high alternating voltage being automatically applied to a sample container in absence of a discharge through the window glazing unit.

The movability of the device means that it is possible to use it in field to analyze gas components inside window units installed in real buildings, not only during the manufacturing of window glazing units. The selectivity of the device to the gas components means that it distinguishes between the components without information about the gas filling obtained *a priori*. The device probes the gas components at normal atmospheric pressure. In order to estimate the operation quality of the window units, the device is capable of recognizing a window unit with more than 10 % of air in addition to a filled noble gas. For determining the performance of the window unit, the device is further capable of discriminating between different possible noble gases (argon, krypton, xenon). In other words, the device is capable of analyzing the gas composition when the gases are argon, krypton, xenon, and air.

Next the invention will be examined in more closely with the aid of a detailed description with reference to the attached drawing.

Brief Description of the Drawings

Fig. 1 is a schematic illustration of one embodiment of the non-invasive device for analyzing the performance of gas-filled window glazing units.

Detailed Description of the Invention

The following description will examine the invention when used in connection of a gas-filled window glazing unit. It should be pointed out that the invention is, however, more

generally applicable to any closed spacings having at least one wall of a transparent or even translucent material. It is required that the material has dielectric properties (rather than conducting properties) to allow for the creation of a discharge by high voltage. Further it is required that the transparent or translucent material allows for transmission of enough emitted light to make spectral recognition possible.

The operation of the non-invasive device according to the present invention is based on discharging the spacing between the panels of a closed spacing, in the following the window panels of a glazing unit by applying rapidly alternating electrical field, collecting and analyzing the emitted light in different spectral intervals in comparison with integral value of the emittance. Rapidly alternating electrical field is known to produce mainly excitation of neutral particles, and ionization as well as dissociation are of minor importance. In discharge, the excited atoms and molecules emit light which is collected and analyzed.

The spectral properties of the emitted light reflect the gas composition in the discharged spacing. In particular, there are a number of known characteristic lines for different elements, and they can be chosen, for example, as 812 nm for argon, 587 nm for krypton, and 467 nm for xenon. These characteristic lines are well separated from each other so that they can be selected by ordinary interference filters. Molecular species, which are specific for air, emit vibrationally structured spectrum, in much broader spectral interval, and they provide mainly emittance signal in integral when no spectral selection is used. These dramatic spectral differences in emission of the species of interest construct the fundamental basis for the invention. By comparing the intensities emitted in different spectral intervals with the integral intensity the gas composition in the discharged volume can be calculated.

In order to create the discharge, two electrodes, an internal (conducting layer of the window glazing unit), and external are used. As mentioned above, it is also possible to use a second external electrode as a counter electrode should the glazing unit not be provided with a conducting layer. An important feature of the invention comprises localization of the discharge, which is achieved by employing an electrode having a small area at least in two

dimensions. Examples of such electrodes are electrodes having an elongated body with a tapered end. The area of the end is preferably less than 10 mm, in particular about 1 mm in diameter. Other examples are conductive layers having a corresponding small area. Such conductive layers can be deposited on the surface of the lens used for collecting the emission. In this case, the discharge starts in the vicinity of the end of the electrode. This localization allows reliable collecting the emitted light to be provided without routine adjustment of the optical system. In the present invention, microlenses can be used to collect the light from the discharge, and the collected light can be transported to light detectors by using fiber optics. It is important that splitting the light to different beams is done after the optical fiber but not from the discharge, which eliminates any influence of natural instability of the discharge geometry.

The processing of the spectral data obtained will be dealt with more closely in relation to the practical embodiment of Figure 1.

Within the scope of the present invention, the term "local" or "localized" discharge means that the discharge takes place in only a part of the closed spacing of interest. As a practical matter, the localized discharge means that the collection of the emission is carried out from a collecting area larger than the emission area.

Turning now to the embodiment depicted in Figure 1, it can be noted that the gas mixture 1 to be analyzed is kept inside the window glazing unit. The window glazing unit particularly contains two glazing panels 2a and 2b. The internal surface of one of the panels, specifically 2a, is covered by the layer, which conducts electrical current, and the other panel (2b) is free of conducting coating.

The non-invasive device depicted in the drawing for analyzing the performance of gas-filled window glazing units comprises a needle-like electrode 5 for applying rapidly alternating high voltage to the spacing of the window glazing unit, a lens 4a for collecting the emitted light, and an optical fiber 6 for transporting the collected light. These parts of the device can be fitted into a first module, which can be called a remote sensor unit 16. The device further comprises a processing unit (or measuring and displaying unit) 15 with

a lens 4b for collimating the transported light, beam splitters 8a, 8b, 8c and 8d for splitting the collimated light beam, one normalizing light detector 9a for measuring a signal proportional to the integral discharge emittance, three component light detectors 9b, 9c and 9d with means 17b, 17c and 17d for spectral selection of different characteristic lines of gas components, data processing means 10b, 10c and 10d for comparing signals in the different channels to estimate gas composition in the window glazing unit, a processor 12, means 11 for detecting the existence of the discharge, means 13 for displaying the obtained information, means 7 for creating a rapidly alternating high voltage, and a switcher 14.

The apparatus is operated as follows. Rapidly alternating electrical field is applied to the window glazing unit from the side of the panel 2b by using the needle-like electrode 5. As the other electrode, the conducting layer of the panel 2a is used. The rapidly alternating electrical field produces a discharged channel in the spacing between the glazing panels, and the discharge starts in the close vicinity to the end of the electrode 5. Emitted light is collected by a lens 4a. The end of the electrode 5 is located at about 1 to 3, preferably about two focal distances of the lens 4a from the lens 4a. The collected light is directed into the optical fiber 6, the end "a" of which locates at about two focal distances from the lens 4a and about at a discharge-lens axis.

The light, transmitted by the optical fiber 6 and emitted from the end "b" of the optical fiber 6, is then collimated by a lens 4b. The lens 4b is located at about 0.5 to 2, preferably about one focal distance from the end "b" of the optical fiber 6. Quasi-parallel light beam goes through a sequence of four beam splitters 8a, 8b, 8c, and 8d. Deflected beams are directed onto light detectors 9a, 9b, 9c, and 9d. The light detector 9a measures intensity proportional to the integral intensity of the discharge. The light beams directed to light detectors 9b, 9c, and 9d are spectrally selected by spectral filters 17b, 17c, and 17d to measure signals proportional to gas component percentage. The electrical signal from the light detector 9a is applied to comparing units 10b, 10c and 10d to generate ratios of the spectrally selected and integral signals. Also, the electrical signal from the light detector 9a is applied to a level unit "Yes-No" 11 to check the appearance of the electrical discharge 3 in the spacing of the window glazing unit. Electrical signals from the level unit "Yes-No"

11 and from the comparing units 10b, 10c and 10d are applied to a processor 12 to be analyzed. The result of the analysis by the processor 12 is shown at a display 13. In particular, the following information is to be displayed: existence of the discharge, type of dominating filling (argon, krypton, xenon), percentage of the dominating filling. The alternating high voltage to apply to the electrode 5 is created by a high-voltage generator 7. The operation of the device is started and stopped by a switcher 14.

Although not shown in Figure 1, the measuring and displaying unit 15 is electrically supplied either from the electrical network or from a battery. The light detectors 9a, 9b, 9c, and 9d include corresponding pre-amplifiers (not depicted) to construct proper electrical signals.

In addition to the numerous advantages of the invention explained above it should be pointed out in connection with the practical embodiment of Figure 1 that it removes the need for calibration of absolute luminescence flux because the device analyzes the ratios between fluxes in spectral interval with normalization by integral flux. Another important feature of the present embodiment is that there is no need in geometrical stability of the measurement because the device analyzes the ratios between fluxes in spectral interval with normalization by integral flux, and optical alignment with required accuracy is prepared at the manufacturing stage. Practically, this means the opportunity of movable performance of the device.

It is understood that many changes and additional modifications are possible in view of different versions of performance without departing from the scope of the inventions as defined in the appended claims. A combination of the claims produces additional advantage.

In particular, it is also possible to mount the means for displaying the obtained information about performance of the window glazing unit in the remote sensor unit formed by the means for locally applying rapidly alternating high voltage and the lens.

The means for measuring gas component signals can comprise a CCD camera.

As briefly discussed above, the apparatus can also contain a sample container for controlling the operational performance of the apparatus as a whole. The sample container is preferably installed into the remote sensor, which is provided with an additional light detector and connected with the data processing means, whereby the apparatus can be operated so that a high alternating voltage is automatically applied to the sample container in the absence of a discharge through the window glazing unit.

The means for splitting the collimated beam and spectrally selecting the characteristic lines can comprise a spectrometer.

Claims:

1. A non-invasive method for selectively determining the concentration of at least one gas component in a gas mixture contained in a closed spacing (1) having at least one transparent, dielectric wall (2a, 2b), comprising:
   - locally applying rapidly alternating high voltage to the spacing to provide localized light emission (3) in an emission area;
   - collecting emitted light of the local emission (3) from a collection area larger than the emission area;
   - determining the integral intensity of the emission;
   - determining the intensity of a spectral interval corresponding to the gas component of interest;
   - calculating the ratio between the intensity of the spectral interval and the integral value of the intensity; and
   - determining the concentration of the gas component from said ratio.

2. The method according to claim 1, wherein the spacing (1) comprises two glass walls formed by two glass sheets (2a, 2b) spaced apart from each other.

3. The method according to claim 2, wherein the spacing comprises a gas-filled window glazing unit (1).

4. The method according to claim 1, wherein a grounded counter-electrode is used.

5. The method according to any of claims 1 to 4, wherein alternating high voltage is applied to the closed spacing using an elongated electrode (5) having a tapered end and by directing said end of the electrode against the closed spacing.

6. The method according to any of claims 1 to 5, wherein the light of the local emission is collected with a lens (4a) to provide a collimated light beam, said lens being located at a distance of about 0.5 to 2 focal distances from the site of the local emission.

7. The method according to claim 6, wherein the collimated light beam is splitted to provide a first splitted beam having a signal proportional to the integral discharge emittance and a second beam which is used for measuring a signal proportional to the concentration of one gas component, said splitted signals being subjected to spectral filtration to measure signals proportional to specific gas components..

8. The method according to claim 7, wherein the collimated light beam is splitted to provide at least one further splitted signal used for measuring signals proportional to the concentration of at least one further gas component.

9. An apparatus for non-invasive analysis of gas-filled window glazing units (1) for determining the performance thereof, comprising:

- means (7) for creating rapidly alternating high voltage,
- means (5) for locally applying the rapidly alternating high voltage to the spacing of the window glazing unit to achieve local emission;
- means (4a, 6, 4b) for collecting and transporting emitted light;
- means (9a) for determining the integral intensity of the emission;
- means (9b-9d) for determining the intensity of a spectral interval corresponding to the gas component of interest;
- means (10b-10d) for calculating the ratio between the intensity of the spectral interval and the integral value of the intensity; and
- means (12) for determining the concentration of the gas component from said ratio.

10. The apparatus according to claim 9, wherein the means for locally applying rapidly alternating high voltage comprise a needle-like electrode (5).

11. The apparatus according to claim 9, wherein the means for locally applying rapidly alternating high voltage comprise a conductive layer coated on the means for collecting the emitted light, which can be used as an electrode.

12. The apparatus according to claim 9, wherein the apparatus contains a second electrode, which can be grounded and set on the opposite side of the window unit.

13. The apparatus according to any of claims 9 to 12, wherein the means for collecting and transporting the emitted light comprise a collecting lens (4a) which can be brought in the vicinity of the closed spacing.

14. The apparatus according to claim 13, wherein the means for collecting and transporting the emitted light further comprise optical fibres (6) for transporting the light and a collimating lens (4b) for collimating the light transported by the optical fibres.

15. The apparatus according to claim 14, wherein the optical fiber (6) comprises optical connectors for connecting to the collecting lens (4a), to the collimating lens (4b) and/or to another optical fiber.

16. The apparatus according to any of claims 13 to 15, wherein the means for collecting and transporting the emitted light (4a, 6, 4b) are formed as a single non-adjustable block (16).

17. The apparatus according to claim 13, wherein the means (5) for locally applying rapidly alternating high voltage and the lens (4a) are fitted together to form a separate sensor unit.

18. The apparatus according to any of claims 9 to 17, comprising means (8a-8d) for splitting the collimated light into a first splitted beam having a signal proportional to the integral discharge emittance and at least one second beam for measuring a signal proportional to the concentration of one gas component.

19. The apparatus according to any of claims 9 to 18, wherein the means for determining the intensity of a spectral interval corresponding to the gas component of interest comprise light detectors (9b-9d) with means (17b-17d) for spectral selection of different characteristic lines of gas components.

20. The apparatus according to claim 19, wherein the means for spectral selection comprise interference filters (17b-17d).

21. The apparatus according to claim 20, wherein the interference filters (17b-17d) have central wave lengths at 467 nm, 587 nm and/or 812 nm.

22. The apparatus according to any of claims 19 to 21, wherein the means for measuring gas component signals are performed as a CCD camera.

23. The apparatus according to any of claims 9 to 22, wherein the apparatus contains a sample container for controlling the operational performance of the apparatus as a whole.

24. The apparatus according to any of claims 9 to 23, further comprising

- data processing means (12) for comparing signals in order to estimate gas composition in the window glazing unit; and
- means (13) for displaying the obtained information.

25. The apparatus according to claim 23, wherein the means for splitting the collimated beam and spectrally selecting the characteristic lines comprise a spectrometer.

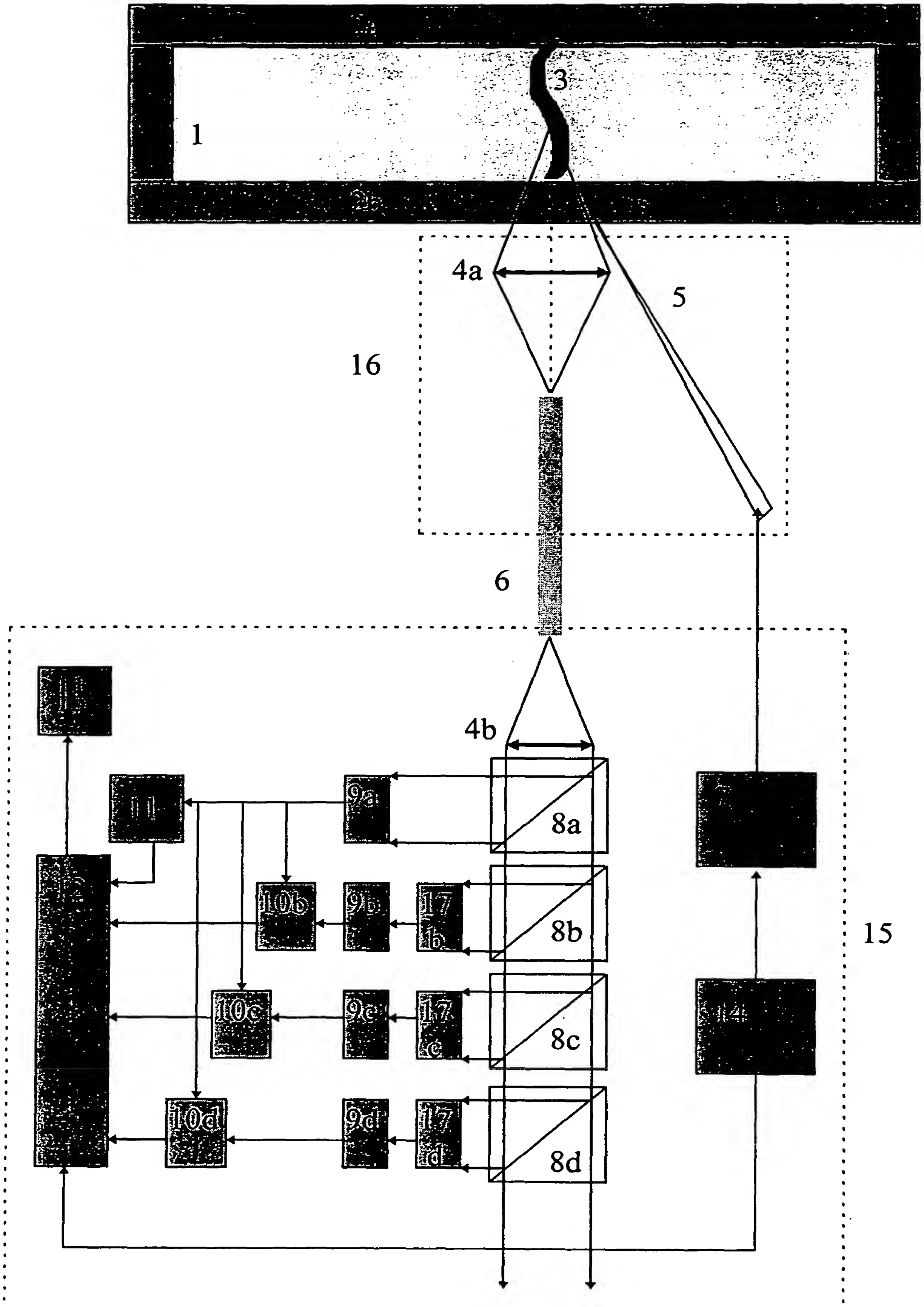
26. The apparatus according to claim 22, wherein the means (13) for displaying the obtained information about performance of the window glazing unit is mounted in the remote sensor unit (16) formed by the means for locally applying rapidly alternating high voltage and the lens.

27. The apparatus according to claim 26, wherein the sample container is installed into the remote sensor (4a, 6, 4b), which is provided with an additional light detector and connected with the data processing means (12), whereby the apparatus can be operated so that a high alternating voltage is automatically applied to the sample container in the absence of a discharge through the window glazing unit.

22 1

(57) Abstract:

A non-invasive portable apparatus for analyzing the performance of gas-filled window glazing units is disclosed. The operation of the apparatus is based on discharging the spacing between the panels (2a, 2b) of the window glazing unit 1 by applying rapidly alternating electrical field to the spacing between the panels of the window glazing unit, on collecting and analyzing the emitted discharge light in different spectral intervals in comparison with integral value of the discharge light. The discharge is created by a needle-like electrode (5), and the inner conducting layer (2a) of the glazing unit serves as another electrode. The localization of the discharge in the vicinity of the end of the needle-like electrode (5) makes it possible to collect the emitted light without routine adjustment of the optical system. In this case, factory-adjusted lenses (4a) can be used to collect the light from the discharge, and the collected light can be transported to light detectors (9a-9d) by using fiber optics (6), which eliminates influence of instability of the discharge geometry.



1
3
4a
5
16
6
4b
8a
8b
8c
8d
15